Chemistry

Theory Notes of
Solid State

In solid state atoms, ions or molecules are arranged orderly in a three dimensional manner due to strong binding forces.

Due to this arrangement, solids acquired rigidity and definite geometric shapes or crystalline structures.

Characteristic properties of the solid state

i)They have definite mass, volume and shape.

ii)Interemolecular distances are short

iii)Intermolecular forces are strong

iv)Their constituent particles (atoms, molecules or ions) have fixed positions and can only oscillate about their mean positions.

v)They are incompressible and rigid

* The existance of a substance in more than one solid modification is called polymorphism.

Amorphous & Crystalline Solids :

Crystalline Solid :

➢ A solid which has a definite and regular geometry due to definite and orderly arrangement of molecules or atoms or ions in three dimensional space is called Crystalline Solid. Crystalline solids are also called true solids. Ex:- Quartz is a crystalline form of silica.

Amorphous Solid

➢ A solid which does not have any pattern of arrangement of molecules or atoms or ions and, therefore, does not have any geometrical shape is called Amorphous Solid. Amorphous solids are also called super colled liquids (or) pseudo sollids. Ex : Glass

Distinction between crystalline and amorphous solids

Property	Crystalline solids	Amorphous solids
Shape	Definite characteristic geometrical shape	Irregular shape
Condition of formation	Slow cooling without disturbing the liquid	Rapid cooling with churning of disturbance
Melting point	Melt at a sharp and characteristic temperature	Gradually soften over a range of temperature
Cleavage property	When cut with a sharp edged tool. They split into two pieces and the newly generated surfaces are plain and smooth	When cut with a sharp edged tool. They cut into two pieces with irregular surfaces
Heat of fusion	They have a definite and characteristic heat of fusion	They do not have definite heat of fusion
Anisotropy	Anisotropic in nature	Isotropic in nature
Order in arrangement of constituent particles	Long range order	Only short range order

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Chemistry By AKS Sir   Theory Notes

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Annealing

➢ An amorphous substance, on heating at a certain temperature, may attain crystalline nature while on colling regains its amorphous nature. This phenomenon is called annealing. Ex : Glass on keeping in semi-solid state for a long time or on cooling, it melts very slowly, it becomes opaque due to development of crystals in it.

Isotropy

➢ Amorphous solids on the other hand are isotropic in nature. It is because there is no long range order in them and arrangment is irregular along all the directions. Therfore, value of any physical property would same along any direction.

Anisotropy

➢ Crystalline solids are anisotropic in nature, that is, some of their physical properties like electrical resistance or refractive index show different values when measured along different directions in the same crystals. This arises from different arrangement of particles in different directions.

Classification of Crystalline Solids

A crystal is classified as ionic, covalent , metallic and molecular according to the nature of the building units, chemical bonding and the intermolecular forces in the crystal.

The characteristics of various types of solids are given in the table.

Molecular Solids :

Molecular solids are subdivided into

➢ (a) Non - polar molecular solids

In these solids molecules are held by weak dispersion forces or London forces or Vander waal forces

Ex:- Solid Ar, He, H_2, Cl_2 and I_2 ,

(b) Hydrogen bonded crystals

Crystals of H_2O, HF, NH_3 and amino acids are some examples of hydrogen bonded crystals.

➢ c) Polar molecular solids

Substances having polar covalent bonds like HCl, SO_2 .

Ionic solids: Ions are the constituent particles of ionic solids. Such solids are formed by the three dimensional arrangements of cations and anions bound by strong coulombic (electrostatic) forces. These solids are hard and brittle in nature. They have high melting and boiling points. In these ions are not free to move. So these are acts as insulators. But in the molten state or when

dissolved in water, the ions become free to move and they conduct electricity.

Metallic solids: Metals are orderly collection of positive ions surounded by the held together by a sea of free electrons. These electrons are mobile and are evenly spread out through out the crystal. Each metal atom contributes one or more electrons towards this sea of mobile electrons. Metals are acts as good electrical and thermal conductors due to the presence of free electrons. Another important characteristic of metals is their lustre and colour in certain cases due to the presence of free electrons. Metals are highly malleable and ductile.

Covalent or Network Solids: Crystalline solids of non-metals result from the formtion of covalent bonds between adjacent atoms throughout the crystal. They are also called giant molecules. Covalent bonds are strong and directional in nature, therefore atoms are held very strongly at their positions. Such solids are very hard and brittle. They have extremely high melting points. They are insulators and do not conduct electricity. Diamond and silicon carbide are typical examples of such solids. Graphite is soft and a conductor of electricity. Graphite has layer liked structure. It is good solid lubricant. In Graphite the distance between two adjacent layers is 340pm. C-C bond length 141.5pm.

Applications of amorphous solids.

➢ Amorphous solids are used in domestic constructions or appliances like photo voltaic cells where the sun light is transformed into electricity.

➢ *Space Lattice (or) Crystall Lattice:* A space lattice is an array of points showing how molecules, atoms or ions are arranged at different sites in three dimensional space.

DIFFERENT TYPES OF SOLIDS

S No	Type of solid	Constituting unit	Interparticle forces	Examples	Physical state	Electrical properties
1.	Molecular solids					
(i)	Polar molecular solids	Polar molecules	Dipole, dipole attraction forces	HCl, SO_2 etc	Soft solid with low m.pt	Insulator
(ii)	Non-polar molecular solids	Non-polar molecules	vander Waals's forces of attraction	$BeCl_2, S_8, P_4$, $I_2, F_2, CH_4,$ CO_2 napthalene etc.	Soft solid with very low m.pt	Insulator
(iii)	H-bonded solids	Molecules capable to form H-bonds	h-bonds	NH_3, ice glucose etc.	Harder than (i) and (ii), with low m.pt	Insulator
2.	Covalent or network solids	Atoms	Covalent bonds	Diamond, quartz, silica B, black P, AlN BN etc. graphite	Very hard high m.pt. rigid, brittle Soft	Insulator Conductor
3.	Ionic solids	Cations and anions	Electrostatic forces of attraction	$NaCl, KNO_3,$ $CuSo_4, 5H_2O,$ $CaF_2, ZnS,$ K_2SO_4 etc.	Hard rigid, brittle, high m.pt	Conductor in fused state or in solution (some solid conductors are also known like AgCl)
4.	Metallic solids	Metal atom (kernels embedded in sea of electrons)	Metallic bonds	Metals Cu, Ag, Mg, Fe	*Hard but malleable and ductile*	Conductor

➤ **Lattice Point:** The point that represents a molecule, an atom or an ion in a space lattice is called Lattice point.

Unit Cell

➤ The smallest portion of the crystal lattice which can be used as repetitive unit in three dimensional manner to get entire crystal lattice is called unit cell. Unit cells are broadly divided into two categories, primitive and centred unit cells.

(a) Primitive unit cells :

➤ When constituent particles are present only on the corner positions of a unit cell, it is called as primitive unit cell.

(b) Centred unit cells : When a unit cell contains one or more constituent particles present at positions other than corners in addition to those at corners, it is called Centred unit cell. Centred unit cells are of three types:

(i) Body-centred unit cells : Such a unit cell contains one constituent particle (atom, molecule or ion) at its body-centre besides the ones that are at its corners.

(ii) Face-centred unit cells : Such a unit cell contains one constituent particle present at the centre of each face, besides the ones that are at its corners.

(iii) End-centred unit cells : In such a unit cell, one constituent particles is present at the centre of any two opposite faces besides the ones present at its corners.
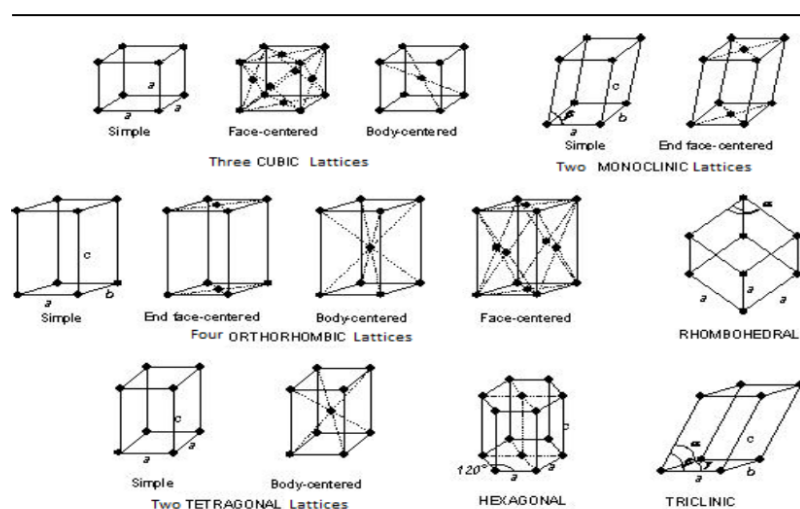
- **The three cubic lattices :** all sides of same length, angles between faces all 90^0.
- **The two tetragonal :** one side different in length to the other, two angles between faces all 90^0.
- **The four orthorhombic lattices :** unequal sides, angles between faces all 90^0.
- **The two monoclinic lattices :** unequal sides, two faces have angles different to 90^0.
- **Hexagonal lattice :** one side different in length to the other two, the marked angles on two faces are 60^0.
- **Rhombohedral lattice :** All sides of equal length, angles on two faces are less than 90^0.
  Triclinic lattice : Unequal sides a, b, c are unequal angles with non equal to 90^0.

  Bravais Lattices
- Bravais showed that there are 14 different possible kinds of three dimensional lattices.
- The geometric shape of the crystal lattice must be same as that of solid crystal itself.
  Ex : If unit lattice is having cubical structure the crystal is also a cube.
- From fundamental laws of crystallography there are 14 basic arrangements known as Bravais Lattices.
- The following are characteristics of a crystal lattice
  a) Each point in a lattice is called lattice point or lattice site.
  b) Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule or an ion.
  c) Lattice points are joined by straight lines to bring out the geometry of the lattice.

- These 14 Bravais lattices are grouped into seven crystal system based on unit cell symmetry. These seven crystal systems are

Crystal System	No. of Bravais lattices	Common names of these lattices
Cubic	3	Simple cubic, fcc and bcc
Tetragonal	2	Primitive; body centred tetragonal prisms
Rhombic	4	Primitive, body centred, face - centred and endcentred
Hexagonal	1	Primitive Hexagonal prism
Trigonal	1	Rhombohedral (or) primitive
Monoclinic	2	Primitive & end centered
Triclinic	1	Triclinic primitive(or) primitive

(c) **CRYSTAL SYSTEMS :-**
A unit cell is characterised by :
(i) its dimensions along the three edges, a, b and c. These edges may or may not be mutually perpendicular.
(ii) angles between the edges, α (between b and c) β (between a and c) and γ (between a and b). Thus, a unit cell is characterised by six parameters, a, b, c, α, β and γ.
- There are 230 crystal forms possible. These forms may be classified into 32 classes on the basis of their symmetry.

➢ On the basis of inter facial angles and axes crystal systems are 7 types.

The crystal structures depends on the set of crystallographic parameters
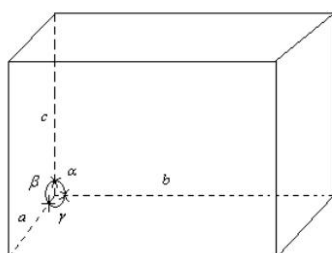
System	Axial angular characteristics	Examples of common substance	Symmetry elements possible
Cubic	$a = b = c$; $\alpha = \beta = \gamma = 90^0$	*NaCl* Diamond Pb, Hg, Ag; Alum Zns; CaF$_2$; FeS$_2$	Four 3 folds axis Six 2 folds axis
Tetragonal	$a = b \neq c$; $\alpha = \beta = \gamma = 90^0$	SnO$_2$, TiO$_2$, white Sn, NiSO$_4$ K$_4$[Fe(CN)$_6$]	One 4 fold axis
Ortho rhombic or rhombic	$a \neq b \neq c$; $\alpha = \beta = \gamma = 90^0$	KNO$_3$; MgSO$_4$.7H$_2$O α – S; K$_2$SO$_4$; BaSO$_4$, PbCO$_3$	Three 2 fold axis 2 fold axis Two Perpendicular planes
Hexagonal	$a = b \neq c$; $\alpha = \beta = 90^0$ $\gamma = 120^0$	Graphite, ice Quartz, Mg, Zn, HgS; PbI$_2$	One 6 fold axis
Trigonal or Rhombo hehral	$a = b = c$; $\alpha = \beta = \gamma \neq 90^0$	Calcite; NaNO$_3$; KMnO$_4$, Bi, Sb; As	One 3 fold axis
Monoclinic	$a \neq b \neq c$; $\alpha = \gamma = 90^0$ $\beta \neq 90^0$	Monoclinic S; CaSO$_4$.2H$_2$O; Na$_2$SO$_4$.10H$_2$O; NaHCO$_3$; FeSO$_4$.7H$_2$O	One 2 fold axis one plane
Triclinic	$a \neq b \neq c$; $\alpha \neq \beta \neq \gamma \neq 90^0$	*CuSO$_4$.5H$_2$O* $K_2Cr_2O_7$.H_3BO_3	....

➢ Ice may give hexagonal or trigonal crystals
➢ Quartz may give hexagonal or trigonal crystals

Symmetry in crystals
Plane of symmetry
➢ When an imaginary plane can divide a crystal into two parts such that one is the exact mirror image of the other, then the crystal is said to have a plane of symmetry.
Axis of symmetry
➢ *An* axis of symmetry is a line about which the ➢ A glass plate containing number of thin lines separated by equal distances. The lines on the glass plate are drawn with diamond. The lines on the glass plate can be compared with lattice points in crystal.
Interfacial angle
➢ The angle between any two faces in an unit cell is called Interfacial angle

Calculation of the contribution of lattice points per unit cell of substance.
➢ A three dimensional crystal lattice is built up by the unit cells arranged in three directions .
➢ The unit cells have different shapes depending on the arrangement of the component atom (or) ions in space lattice.
➢ Each lattice point and the component particle contribute fraction to the unit cell because they are shared by vicinal unit cells.

The atoms, molecules (or) ions that are making up the crystal are present at the lattice points and are represented by points.

Unit cell	Contribution of lattice points			Net no.of constituent particles
	Corners (1/8)	Face Center (1/2)	Body Center (1)	
simple cubic unit cell	$8 \times \frac{1}{8} = 1$	-	-	1
Face centered unit cell	$8 \times \frac{1}{8} = 1$	$6 \times \frac{1}{2} = 3$	-	4
Body centered unit cell	$8 \times \frac{1}{8} = 1$	-	$1 \times 1 = 1$	2
End centre unit cell	$8 \times \frac{1}{8} = 1$	$2 \times \frac{1}{2} = 1$	-	2

➢ A lattice point at the corner of a unit cell is shared by 8 vicinal unit cells.
➢ A face centered point is shared by two adjacent unit cells.
➢ A edge centered point is shared by four adjacent unit cells

➤ A body centered lattice point belongs completely to a specific unit cell.

Calculation of density of unit cell

Knowing the unit cell dimensions, the density of a crystalline substance can be calculated from the formula

$$\rho = \frac{ZM}{N_0 a^3} \quad \text{or} \quad \rho = \frac{ZM}{N_0 V} \quad \text{Where} \quad \rho = \text{density}$$

Z = No. of atoms (or) formula units per unit cell
M = Molecular weight of the lattice particle (Atomic wt / formula wt)
a = unit cell length. v = volume

X-Ray study of crystal structure- Bragg's Equation-X-Ray Difraction studies X – RAY STUDY OF CRYSTAL

➤ X – ray diffraction studies of crystal clearly reveal the internal structure of crystals.

➤ The exact pattern of arrangement of crystal components, size and shape of the unit cell.

➤ Electromagnetic radiation propagate in the form of waves in all directions . In the propagation of waves along a direction, the maximum displacement perpendicular to motion of the wave is known as amplitude of the wave.

➤ For constructive interference resultant amplitude is

$2 E_0 \ (E_0 = \text{Amplitude})$

➤ For destructive interference resultant amplitude is Zero

➤ The waves, if present in the same phase they undergo constructive interference on the other hand if the waves are not in phase, they undergo destructive interference.

Bragg's Equation

➤ W.L. Bragg and W.H. Bragg worked out and gave a mathematical relation to determine inter atomic distance from X – ray diffraction pattern. This relation is called the Bragg's equation

$n\lambda = 2d \sin\theta$; n = order of reflection;
λ = Wave length of x-rays
d = interplanar distance, θ = angle of reflection

Order of reflection	n value	Bragg's equation
First order	1	$\lambda = 2d \sin\theta$
Second order	2	$\lambda = d \sin\theta$
Third order	3	$\lambda = \frac{2}{3} d \sin\theta$
n^{th} order	n	$\lambda = \frac{2}{n} d \sin\theta$

➤ As 'n' value increases θ value increases
➤ X – rays of definite wave length obtained from $X - ray$ tube, passes through a slit and falls on a known face of the crystal. The position of the crystal can be read on a scale.
➤ The intensity of the diffracted X – ray from the crystal is measured on a photographic plate or an ionization chamber. The ionization chamber contain CH_3Br vapours.
➤ The extent of ionization in the vapour is shown by the electrometer reading. As the intensity of the diffacted X – rays increases, the degree of ionization also increases
➤ By changing the angle of incidence the extent of ionization at different angles is recorded in the electrometer.
➤ The Crests of the graph, taken from electrometer reflect maximum diffraction. The angles corresponding to the crests are noted from the graphs.
➤ The angles are substituted for 'θ' in Bragg's equation and the values of 'd' are calculated.
Ex : - For NaCl crystal 'd' values are in the ratio

of $1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}} = 1 : 0.707 : 1.154$. From this it is

confirmed that the crystal has F.C.C. structure.
Note : - Bragg's method to be used, large single crystals are necessary. The planes of the crystal must be fully developed and easily identified.
➤ Debye - Scherrer Method is used to determine the crystal structures.

CLOSE PACKED STRUCTURES

Packing of Solids and Voids

➤ In solids constituent particles are arranged as spheres in close structure.
➤ In close packed structure, maximum space is occupied by constituent particles and leave minimum vacant space
➤ When the spheres are closely packed the different crystal systems are generated.
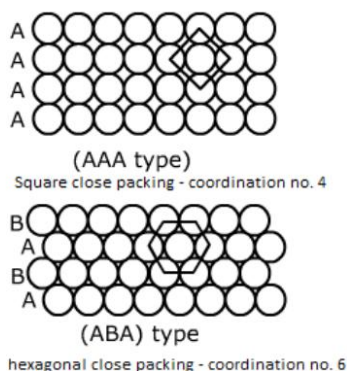**Co-ordination number :** The number of nearest neighbours of a particle is called its coordination number.

A) **Close packing in one dimension :**

Close packing of spheres in one dimension

Co-ordination number is 2.

b) **Close packing in two dimensions :**

(AAA type)
Square close packing - coordination no. 4

(ABA) type
hexagonal close packing - coordination no. 6

c) **Close packing in three dimensions :**

(i) Three dimensional close packing from two dimensional square close-packed layers : While placing the second square close-packed layer above the first we follow the same rule that was followed when one row was placed adjacent to the other. The second layer is placed over the first layer such that the spheres of the upper layer are exactly above those of the first layer. In this arrangement spheres of both the layers are perfectly aligned horizontally as well as vertically. Similarly, we may place more layers one above the other. If the arrangement of spheres in the first layer is called 'A' type, all the layers have the same arrangement. Thus this lattice has AAA.... type pattern. The lattice thus generated is the simple cubic lattice, and its unit cell is the primitive cubic unit cell.

(ii) Three dimensional close packing from two dimensional hexagonal close packed layers. Three dimensional close packed structure can be generated by placing layers one over the other.

➢ **(a) Placing second layer over the first layer:** Let us take a two dimensional hexagonal close packed layer 'A' and place a similar layer above it such that the spheres of the second layer are placed in the depressions of the first layer. Since the spheres of the two layers are alligned differently. This is AB AB type packing.

The sphers of the second layer 'B' are not covered all the triangular voides of the first layer 'A'. This gives rise to different arrangements. Wherever a sphere of the second layer is above the void of the first layer (or vice versa) a tetrahedral void is formed. These voids are called **tetrahedral voids** because a tetrahedron is formed when the centres of these four spheres are joined.

At other places, the triangular voids in the second layer are bove the triangular voids in the first layer, and the triangular shapes of these do not overlap. One of them has the apex of the triangle pointing upwards and the other downwards. Such voids are surrounded by six spheres and are called **octahedral voids**.

Let the number of close packed spheres be N, then :

The number of octahedral voids generated = N
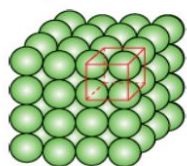*The number of tetrahedral voids generated = 2N*

(b) Placing third layer over the second layer: When third layer is placed over the second, there are two possibilities.

(i) Covering Tetrahedral voids : Tetrahedral voids of the second layer may be covered by the spheres of the third layer. In this case, the spheres of the third layer are exactly aligned with those of the first layer. Thus, the pattern of spheres is repeated in alternate layers. This pattern is often written as ABAB.... pattern. This structure is called hexagonal close packed (hcp) structure. This sort of arrangement of atoms is found in many metals like magnesium and zinc.

(ii) Covering octahedral voids : The third layer may be placed above the second layer in a manner such that its spheres cover the octahedral voids. When placed in this manner, the spheres of the third layer are not aligned with those of either the first or the second layer. This arrangement is called "c" type. Only when fourth layer is placed, its spheres are alligned with those of the first layer. This pattern of layers is often written as ABCABC..... This structure is called cubic close packed (ccp) or face-centred cubic (fcc) structure. Metals such as copper and silver crystallise in this structure.

both these types of close packing are highly efficient and 74% space in the crystal is filled. In either of them, each sphere is in contact with **twelve spheres**. Thus, the coordination number is 12 in either of these two structures.

Interstial Voids :

➤ The empty spaces between the three dimensional layers are known as holes or voids. The holes are also refered as interstices. There are three types of holes possible.

Tetrahedral holes :

➤ A hole formed by three spheres in contact with each other of a layer. The hole is capped by a sphere from an upper layer.(Planar triangle with vertex down wards)

➤ A hole formed by three spheres of a layer in contact with each other and also with a sphere of a next lower layer (planar triangles with vertex upward)

➤ Note : In the above types of holes the four spheres are arranged at the vertices of a regular tetrahedron.

➤ If 'X' spheres form a solid there are a total of '2X' tetrahedral holes.

➤ Radius ratio of tetrahedral void, $\dfrac{r_{void}}{r_{sphere}} = 0.225$.

Octahedral hole : It is the vacant space between a group of three spheres in a layer and another set of three spheres of a next layer. These six spheres surrounding the hole, lie at the vertices of a regular octahedron.

➤ In CCP or FCC lattice, one octahedral void is at the body centre of the cube and one octahedral void at the centre of each of the 12 edges. Hence total number of octahedral voids

$$= 1 + 12 \times \dfrac{1}{4} = 1 + 3 = 4.$$

➤ If there are 'X' atoms in a close packed structure, there are 'X' octahedral holes present.

➤ Thus number of tetrahedral holes is double the number of octahedral holes. The size of these holes depends on the size of the spheres producing them.

➤ Octahedral holes are larger than tetrahedral holes.

➤ Radius ratio of octahedral void, $\dfrac{r_{void}}{r_{sphere}} = 0.414$.

Locating Tetrahedral and Octahedral Voids
Generally close packed structures have both tetrahedral and octahedral voids. Let us take ccp (or fcc) structure and locate these voids in it.

(a) Locating Tetrahedral Voids
Let us consider a unit cell of ccp or fcc lattice. The unit cell is divided into eight small cubes.
Each small cube has atoms at alternate corners. In all, each small cube has 4 atoms. When joined to

each other, they make a regular tetrahedron. Thus, there is one tetrahedral void in each small cube and eight tetrahedral voids in total. Each of the eight small cubes have one void in one unit cell of ccp structure. We know that ccp structure has 4 atoms per unit cell. Thus, the number of tetrahedral voids is twice the number of atoms.

(b) Locating Octahedral Voids
Let us again consider a unit cell of ccp or fcc lattice. This unit cell has one octahedral void at the body centre of the cube. Besides the body centre, there is one octahedral void at the centre of each of the 12 edges. Each edge of the cube is shared between four adjacent unit cells. 1/4th of each void belongs to a particular unit cell.
Thus in cubic close packed structure Octahedral void at the body-centre of the cube=1.
12 octahedral voids located at each edge and shared

between four unit cells $= 12 \times \dfrac{1}{4} = 3$

∴ Total number of octahedral voids = 4
We know that in ccp structure, each unit cell has 4 atoms. Thus, the number of octahedral voids is equal to this number.

Packing Fraction (Density of packing)
Efficiency (or packing fraction or density of packing) of a unit cell is defined in terms of the percentage volume occupied by spheres in that unit cell, out of total available volume. It is calculated by the following formula.
No. of spheres / unit cell x
% efficiency = volume occupied by each sphere / total volume of unit cell x 100

1. **Efficiency of packing in simple cubic unit cell :** A simple cube is having 1 sphere per unit cell. Let consider the edge of a simple cubic unit as

a, then the volume of unit cell is a^3,
we known from the earlier discussion that in simple

cube $a = 2r_s$ where 'r_s' is the radius of sphere.
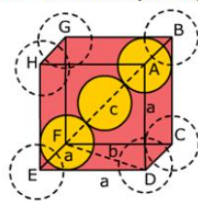Percentage efficiency of simple cubic unit cell = volume of one sphere / volume of unit cell x 100
(or)

$$\dfrac{\frac{4}{3}\pi \times (r_s)^3}{a^3} \times 100 = \dfrac{\frac{4}{3}\pi \times (r_s)^3}{(2 \times r_s)^3} \times 100$$

(or) $\dfrac{\frac{4}{3}\pi}{8} \times 100 = 52.3$

Thus, the volume occupied by sphere in simple cubic unit cell is 52.3% and void volume is 47.7 per cent.

2. **Efficiency of packing in body-centred unit cell :** Consider a body-centred unit cell with edge length 'a' and with radius of sphere 'r_s'. As body centred unit cell is having two spheres per unit cell and a^3 is the volume of unit cell by taking edge length 'a'.

From $\triangle ABC$, $AC = \sqrt{2}a$ and from $\triangle ADC$, $CD = \sqrt{3}a$ and we know

Face diagonal of cubic unit cell is $\sqrt{3}a$

Thus, $CD = 4r_s = \sqrt{3}a$ or $a = \dfrac{4}{\sqrt{3}}r_s$

percentage efficienty of body-centered unit cell = Volume of two sphere / Volume of cube x 100

(or) $\dfrac{2 \times \dfrac{4}{3}\pi(r_s)^3}{a^3} \times 100$

(or) $\dfrac{2 \times \dfrac{4}{3}\pi(r_s)^3}{\left(\dfrac{4}{\sqrt{3}}r_s\right)^3} \times 100 = 68.05$

Thus, the volume occupied by spheres in body-centred unit cell is 68.05% and void volume is 31.95%.

3. **Efficiency of packing in face-centred unit cell :** Consider a face-centred unit cell with edge length 'a' and volume a^3. Radius of sphere is taken as r_s. It is clear from the figure that touch with the two other atoms diagonally arranged.
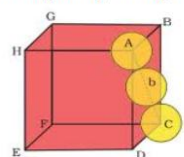
Cubic close packing other sides are not provided with spheres for sake of clarity.

From $\triangle ABC$, ,

$BC = \sqrt{2}a = 4r_s$, (or) $a = \dfrac{4}{\sqrt{2}}r_s = 2\sqrt{2}r_s$

We know that there are four spheres per unit cell in a face-centred unit cell and thus per cent efficiency of face centred unit cell.

= Volume of four spheres / Volume of cube x 100

$= \dfrac{4 \times \dfrac{4}{3}\pi(r_s)^3}{a^3} \times 100$

$= \dfrac{4 \times \dfrac{4}{3}\pi(r_s)^3}{\left(2\sqrt{2}r_s\right)^3} \times 100 = 74.06$

Thus, the volume occupied by spheres in face-centred unit cell (ccp arrangement) is 74.06% and void volume is 25.94%.

➢ Length of face diagonal - $\sqrt{2}a$
➢ Length of body diagonal - $\sqrt{3}a$
➢ For fcc lattice of an ionic crystal of NaCl type edgelength, $a = 2(r_c + r_a)$
➢ For bcc lattice of an ionic crystal edgelength $\sqrt{3}a = 2(r_c + r_a)$

Radiusratio $\left[\dfrac{r_{Small}}{r_{large}}\right]$:-

It is the ratio of the smaller ion radius to that of the larger ion i.e. $\left[\rho = \dfrac{r_{small}}{r_{large}}\right]$

In many cases r_{small} is the cation radius and r_{large} is that of anion. The shape of the crystals depends on coordination number.

Radius Ratio	Shape of Crystal	Coordination Number
Upto 0.15	Linear	2
0.15 to 0.225	Trigonal planar	3
0.225 to 0.414	Tetrahedral	4
0.41 to 0.73	Square planar	4
0.414 to 0.732	Octahedral	6
>0.73	Cubic	8

Coordination Number of Crystals:
The coordination number of an atom or ion in solid is the number of nearest neighbours for that atom or ion

Eg :1) In $NaCl$ crystal, coordination number of Na^+ ion as well as Cl^- ion is 6.
2) Coordination number of C in diamond is 4

3) In SiO_2, coordination of Si is 4 while that of oxygen atom is 2

4) In metal lattices the coordination number of a metal atom is usually 8 or 12.

Bonding in metallic solids :

Any theory which is proposed to explain bonding in metals must be capable of explaining the following.

➢ Bonding between atoms of the same element and (i.e identical atoms) between atoms of widely differing metals and bonding in. alloys.

➢ Should not involve directional bonding

➢ The properties of metals in solutions and in liquid states etc.

➢ The mobility of electrons.

(a) **Electron Sea model**

➢ It was initially proposed by Drude and refined by Lorentz. It is known as Drude – Lorentz theory.

➢ According to this theory, The force that binds a metal ion to the mobile electrons within its sphere of influence is known as metallic bond.

➢ The formation of metallic bond involves

➢ A metal lattice comprises of rigid spheres of metal ions

➢ Each metal atom contributes its valence electrons to the sea

➢ These electrons move freely in the lattice free spaces i.e. interstices

➢ Cohesive forces result from electrostatic attractions between the positive metal ions and the electron cloud.

➢ It explains electrial conductivity and metalic lustre

Defects

➢ Failed to explain quantitative calculations for the lattice energies of ionic compounds.

(b) Valence bond theory of metals

It was proposed by Linus Pauling. This theory is also referred as Resonance theory. According to this theory,

➢ The metallic bond is essentially a polar or a non polar covalent bond.

➢ The covalent bond involves resonance between a number of structures having one electron and electron pair bonds.

➢ Resonance occurs due to the possibility of insufficient valence electrons for the formation of electron pair bonds with each atom of the metal. Resonance not only involves covalent bonds but also ionic linkages.

Defects

➢ does not explain the conduction of heat

➢ Metallic lustre

➢ Retention of the metallic properties in either the liquid state or in the solution.

dimensional hexagonal close packing.

Point defects in Crystals

➢ Stoichiometric compounds are called Daltanides, non-stoichiometric compounds are called Berthollides.

➢ Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance

➢ Properties like density, entropy and heat capacity are influenced by crystal defects to a lesser extent.

➢ The defects in the crystal, influence the properties like mechanical strength, electrical conductivity and chemical activity of the solids to a greater extent.

➢ Thermodynamically all solids possess a tendency to acquire defects because defects result in disorder and hence increase the entropy of the system

➢ Electron micro scope is used to know the defects in a solid crystal

➢ The defects in the crystals can be divided in to different kinds

Types of Crystal defects

➢ **Intrinsic defects :** These are seen in pure crystals

Extrinsic defects

➢ These are due to the impurities in the solids

Point defects :

➢ These occur at the lattice points or sites in the crystals

Extended defects

➢ These are present in one or more dimensions

In stoichiometric compounds two types of defects are observed

Stoichiometric defects

➢ They are also called intrinsic or thermodynamic defects. These are of two types. 'Vacancy defect' and 'interstitial defect'. When some of the lattice sites are vacant, the crystal is having vacancy defect. When some constituent particles occupy an interstitial site, the crystal is having interstitial defect. They are shown by non-ionic solids.

➢ Ionic solids show.

a) Schottky defect

(Schottky-Wagner defects)

➢ This defect arises due to a vacancy at cation sites and equal number of vacancies at anion sites

➢ In ionic crystals electrical neutrality is to be maintained

➢ This type of defect occurs in ionic compounds with
(a) High co-ordination numbers and
(b) Where the positive and negative ions are of similar

size i.e., $\dfrac{r^+}{r^-} \cong 1$

Ex : NaCl, CsCl

➤ Schottky defect is found in highly ionic compounds
➤ Large number of vacancies in the lattice lower the density

b) Frenkel defect

➤ This type of defect arises due to a vacancy at a cation site. Actually, The cation moves to another position between two layers (intersticial position) and it is surrounded by a greater number of anions
➤ Frenkel defect is favoured by a large difference in sizes between cation and anion

➤ Compounds having ions of different sizes i.e $\dfrac{r^+}{r^-}$ is low since positive ions are smaller than negative ions, generally the positive ions are found in interstitial positions
➤ In these compounds the coordination number is low(usually 4 or 6)
Ex : ZnS, AgBr, AgI, AgCl.
➤ Some ionic crystals have both the Schottky as well as Frenkel defects **Ex :** AgBr
➤ Frenkel defects do not change the density of solids.

c) Impurity defect :-

If molten NaCl containing small quantity of SrCl₂ is crystalised, some of the Na⁺ ions are replaced by Sr⁺². Each Sr⁺² replaces two Na⁺ ions. It occupies the site of one Na⁺ ion and the other site remains vacant. Other example is the solid solution of CdCl₂ and AgCl.

Non Stoichiometric point defects :
They include
Metal excess defect (Due to anion vacancy)
: It is due to absence of anion from littice site leaving a hole which is occupied by electron to maintain electrical neutrality

| A⁺	B⁻	A⁺	B⁻
B⁻	A⁺	e⁻	A⁺

F - Centres :
➤ Holes occupied by electrons are called F - Centres (Colour centres). The greater the number of F - centres the greater is the intensity of colour of solid and solids are paramagnetic in nature due to F - centres
Eg : NaCl is yellow, KCl is violet, LiCl is pink
Crystals showing schottky defect also show this defect.
Metal excess defect due to the presence of extra cations at interstital sites :-
➤ ZnO on heating loses oxygen and turns yellow. Now there is excess of Zinc in the crystal. The excess Zn⁺² ions move to interstitial sites and the electrons to neighbourning interstitial sites.

$$ZnO \xrightarrow{heating} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$
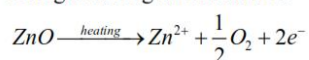
Metal deficiency defect due to cation vacancy :
➤ It is due to absence of a metal ion from its lattice site and charge is balanced by ion having higher positive charge.

A⁺	B⁻	O	B⁻
B⁻	A⁺⁺	B⁻	A⁺

Transition metals exhibits this defect. A typical example of this type is FeO which is mostly found with a composition of $Fe_{0.95}O$. It may actually range from $Fe_{0.93}O$ to $Fe_{0.96}O$. In crystals of FeO some Fe^{+2} cations are missing and the loss of positive charge is made up by the presence of required number of Fe^{+3} ions.

Electrical and Magnetic properties
➤ Properties of solids depending on the nature of bonding or cohesive forces present in them
➤ In ionic solids cohesive forces are due to the lattice energy and they originated from Coulombic forces of attractions between the two ions
➤ In metals electrons are essentially mobile and so the properties of metals can be explained in terms of electron bands formed by molecular orbitals.
➤ Crystals can possess various structures, these structures can be studied by X-ray diffraction methods.
➤ Pure crystalline solids are also imperfect arrangements. These defects in solids cause changes in the properties of the solids.
➤ Crystalline solids exhibit a wide range of properties namely, Electrical, Mechanical, Magnetic and other properties.
➤ The physical properties of solid, its structure and its chemical composition are all closely interrelated.

Electrical Properties :
➤ Based on electrical conductivity, solids can be broadly classified into three types
➤ They are Metals, Semi-conductors and Insulators or Non-conductors
➤ Metals are conductors and have conductivity of the order of 10⁴ to 10⁷ ohm⁻¹m⁻¹
➤ Insulators have very low conductivity of the order of 10⁻²⁰ to 10⁻¹⁰ ohm⁻¹m⁻¹
➤ The solids whose conductivity lies between those of Metallic conductors and insulators are called Semi-conductors. The order of conductivity of semi - conductors is 10⁻⁶ to 10⁴ ohm⁻¹m⁻¹
➤ The electrical conductivity that is observed is usually related to defects in the crystal.
➤ In such defective crystal the migration of ions or charge imperfections(in case of Ionic conductivity) or the motion of electrons and shifting of holes(increase of electronic conductivity) relate the conductivities.

➢ The mechanism of electrical conductivity may be given in terms of
a) Vacancy Mechanism b) Interstitial Mechanism and c) Interstitialcy Mechanism

➢ The Magnitude of electrical conductivity strongly depends on the number of electrons available to participate in the conduction process.

➢ In Metals the conductivity depends on the number of valence electrons present per atom.

➢ when a large number of atoms unite their wave functions interact.

➢ This results in a large number of molecular orbitals or energy levels, some Bonding and some antibonding.

➢ These energy levels are closely spaced energy levels and are known as bands.

➢ The number of energy levels is equal to the number of Atomic orbitals interacting.

➢ One half of these resulting orbitals have lowered energy levels and are known as bonding orbitals. They are of similar energies and form a continuous band of orbitals.

➢ The other half of resultant orbitals have raised energy levels are known as Antibonding energy levels or orbitals.

➢ At all real temperatures the band has a large number of half filled energy levels. Electrons can flow readily through these bands only when the band is incompletely filled with electrons or when electronic band(filled energy levels) is very close to vacant molecular orbitals.

➢ At laboratory temperatures the conductivity of the metals is nearly independent of impurities and the lattice defects.

➢ At low temperatures the mobility due to vibrations in the lattice is quite negligible and as a result the conductivity becomes infinitely large.

➢ The conductivity of metals generally decrease with an increase in temperature. This is probably due to increased vibrations in the lattice points the resistance to the flow of electrons increases.

➢ The impurities in the metal and the imperfections in the lattice also contribute to the conductivity.

➢ Measurement of the resistance of the metal as resistance ratio $\rho_{300K}/\rho_{4.2K}$ explain the purity of the metal.

➢ The conductivity of semi conductors varies completely in the opposite way to that of the metals.

➢ Semi conductors conductivities increases with increase in temperature. This is due to the fact that the electrons from the valence band jump to the conduction band.

➢ Pure semi conductors which exhibit this property are known as intrinsic semi conductors.

➢ The temperature zone where the conductivity depends on the thermal electrons and the holes in the lattice of the semi conductors is known as intrinsic region.

➢ At low temperature the conductivity is mainly determined by the concentrations of the electron donors and the acceptors. This region is known as extrinsic region.

Doping

➢ Addition of B $\left(IIIA\,Group\right)$ $\left(or\right)$ P (or) As $\left(VA\,Group\right)$ element to alter the conductivity of $Ge\left(or\right)$ Si is called as doping.

➢ Pure $Si\left(or\right)Ge$ are intrinsic semiconducters

➢ In doping, group $IIIA$ (13 group element) element behaves as electron acceptor and group $VA\left(15group\,elements\right)$ element behaves as donor.

Electron - rich impurties

➢ When VA (or) 15th group element is added to Si, the crystal lattice does not change, but few Si atoms are replaced by group VA (or) 15th group elements, it forms covalent bonds with Si the fifth electron is delocalised, therefore Si becomes electrical conductor.

➢ Silicon doped with VA (or) 15th group element is known as 'n' type semi conductor (n = negatively charged electrons are responsible for conductivity)

➢ In doping, VA (or) IIIA group element is called as dopant

➢ When IIIA (or) 13th group ;element like B (or) Al or Ga or In is added to Si, the substitution of few Si atoms by group $IIIA$ takes place

Electron - deficit impurties

➢ $IIIA$ group element has only 3 valence electrons. One more electron is required, it is left as a vacant place on the atom. This is called as electron vacancy or a hole.

➢ This electron vacancy in the crystal structure migrates from one atom to another. This is responsible for electrical conductivity of Si.

➢ 'Si' doped with IIIA (or) 13th group element is called p – type semiconductor

Applications

➢ n – type and p – type semi conductors both are used in electronic devices
Example : Diode, pnp or npn type semiconductors are used in transistors.

- These transistors are used to detect (or) amplify radio or audo signals

- In the conversion of radiant energy into electrical energy solar cell (p – n type) is used

- Many solid state semiconductors are prepared by combining IIIA or 13th group elements with VA or 15th group elements and IIB or 12th group elements with VIA or 16th group

- In this type of conductors bond is not pure covalent. Nature of the bond depends on electronegativities of two elements.

- Transition metal oxides shows wide variation in this electrical properties.

- Metal sulphides of transition elements also exhibits wide variation in their electrical properties.

Magnetic Properties

Every substance has some magnetic properties associated with it. Each electron in an atom behaves like a tiny magnet. Its magnetic moment originates from two types of motions (i) its spin around its own axis. Electron being a charged particle and undergoing these motions can be considered as a small loop of curent which possesses a magnetic moment. Thus, each electron has a permanent spin and an orbital magnetic moment associated with it. Magnitude of this magnetic moment is very small and is measured in the unit called Bohr magneton

μ_B. It is equal to $9.27 \times 10^{-24} Am^2$.
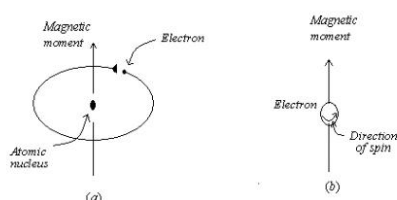
The substances can be classified into five types depending on their response to an applied magnetic field.

- *(a) Diamagnetic Materials :* The substances which are weakly repelled by magnetic field examples NaCl, KCl, TiO_2 ZnO, H_2O Benzene etc.
    Alignment of magnetic moments in diamagnetic substances
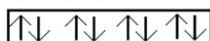
(b) Paramagnetic Materials:

- The substances which are attracted by magnetic field due to the presence lone electrons on atoms, ions or molecules.
  They lose their magnetic property when the applied filed is removed
  Ex : O_2, Cu^{++}, Fe^{+2}, Fe^{+3}, Cr^{+3}, Na, Ti_2O_3, VO_2, NO etc

(c) Ferromagnetic Materials :

- The substances which are strongly attracted by magnetic field.
  These substances contain domains of magnetization. All of them are oriented in the same direction. They retain their magnetism even after withdrawal of applied field.
  Ex : Fe, Co, Ni, CrO_2, Gadalonium etc.

- Fe, Co, Ni, are the only three elements which show ferromagnetism at room temperature.
  The alignment of magnetic moments in these substances is
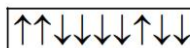

(d) Anti Ferromagnetism :

- It is due to compensatory alignment of moments. The net moment is Zero. The alignment of magnetic moments in these substances is

Ex : MnO_2, V_2O_3, NiO etc.

(e) Ferrimagnetism :

- It is due to the unequal number of alignement of moments in parallel and antiparllel directions. It results in the net moment.

Fe_3O_4 and Ferrites like $MgFe_2O_4$, $CuFe_2O_4$, $ZnFe_2O_4$, $NiFe_2O_4$, etc.

- All the magnetically ordered solids transforms to the paramagnetic state at elevated temperatures due to the randomization of spins
  Ex : V_2O_3 changes to paramagnetic at 150 K and NiO at 523 K
  The substance also lose ferrimagnetism on heating and become paramagnetic.

Dielectric properties

➢ A dielectric is a substance in which an electric field gives rise to net flow of electric charge.

➢ Under the influence of applied field, dipoles are developed in these susbstances.

➢ These dipoles align in two different ways
 a) in such a way that there is a net dipolemoment (non - compensatory way)
 b) in such a way that there is no net dipolemoment (compensatory way)

➢ The crystals in which there is a net dipolemoment when subjected to a stress, produce electricity. It is called piezoelectricity or pressure electricity.

➢ In some piezoelectric solids, dipoles are spontaneously aligned in a particular direction, even in the absence of electric field. They are called 'ferroelectric substances'.
 eg : Barium titanate ($BaTiO_3$), sodium potassium tartarate, potassium hydrogen phosphate (KH_2PO_4) etc.
 In some crystals, the dipoles align in opposite directions, then there is no net dipolement. They are called 'antiferroelectric susbstances'
 eg : lead zirconate ($PbZrO_3$)
 If electricity is produced on heating the crystal then it is called pyroelectricity.

➢ **Applications** : Piezoelectric crystals are used in microphones, ultrasonic generators, sonar detectors, transducers etc.

➢ **Structure of Some simple ionic compounds : It can be summarised in the following table, for cubic ionic solids**

S.No	Crystal Structure	Packing	Cord.No	No.of formula units per unit cell	Examples
1.	Rock Salt (NaCl)	Cl^- in ccp Na^+ in octahedral voids	6	4	Halides of Li, Na K, Rb, AgCl, AgBr NH_4Cl
2.	Zinc blende(ZnS)	S^{-2} in ccp Zn^{++} in alternate tetrahedral voids	4	4	CuX(Cl, Br, I), AgI, BeS tetrahedral voids
3.	Wurtzite (Zns)	Zn^{++} in hcp S^{-2} in alterante tetrahedral voids	4	4	
4.	CsCl	Cs^+ in Cubic Voids Cl^- at the corners of a cube or vice versa	8	1	CsBr, CsI, CsCl, TlCl, TlBr, TlI, TlCN
5.	Fluorite (CaF_2)	Ca^{++} in ccp. F^- in tetrahedral voids	Ca^{++}, F^- (8, 4)	4	SrF_2, BaF_2, $BaCl_2$, CaF_2, CdF_2, PbF_2
6.	Antifluorite (Li_2S)	S^{-2} in ccp, Li^+ in tetrahedral voids	Li^+, S^{2-} (4 ,8)	4	Na_2O, Li_2O, K_2O, Na_2O, K_2S